

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 0 411 628 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
19.11.1997 Bulletin 1997/47

(51) Int Cl.<sup>6</sup>: **C08K 5/00, C08J 7/00,**  
**C08L 23/02**  
// (C08K5/00, 5:13, 5:51)

(21) Application number: **90114853.6**

(22) Date of filing: **02.08.1990**

(54) **Process for the stabilization of polyolefin and products obtained thereby**

Verfahren zur Stabilisierung von Polyolefinen und so erhältliche Produkte

Procédé de stabilisation de polyoléfine et produits ainsi obtenus

(84) Designated Contracting States:  
**AT BE DE DK ES FR GB IT NL SE**

(30) Priority: **02.08.1989 IT 2142389**

(43) Date of publication of application:  
**06.02.1991 Bulletin 1991/06**

(73) Proprietor: **MONTELL NORTH AMERICA INC.**  
**New Castle County Delaware (US)**

(72) Inventors:  
• **Caselli, Giancarlo, Dr. chem.**  
**I-44100 Ferrara (IT)**

• **Gorini, Giuseppe, Dr. chem.**  
**I-44100 Ferrara (IT)**

(74) Representative: **Zumstein, Fritz, Dr. et al**  
**Patentanwälte,**  
**Dr. F. Zumstein,**  
**Dipl.-Ing. F. Klingseisen,**  
**Bräuhausstrasse 4**  
**80331 München (DE)**

(56) References cited:  
**DE-A- 2 260 213** **FR-A- 2 301 558**  
**FR-A- 2 389 652** **JP-A-63 241 048**  
**US-A- 4 377 651** **US-A- 4 463 112**  
**US-A- 4 739 000**

**EP 0 411 628 B1**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

## Description

The present invention relates to a process for the stabilization of olefin polymers in nonextruded particle form with spheroidal geometrical shape, comprising depositing on the surface of said particles a mixture comprising one or more organic phosphites and/or phosphonites, and one or more phenolic antioxidants. Said mixture may also include additional components, particularly light stabilizers, thioethers, organic polysulfides, and diluents.

A method very well known in the field for the stabilization of olefin polymers consists in blending the polymers with the stabilizers in a suitable mixer, including an extruder and extruding the mixture thus obtained. In this manner one obtains pellets in which the stabilizers are distributed in a relatively homogeneous manner, giving good stabilization to the pellets themselves, which can then be transformed into finished products.

The above mentioned techniques of pelletization by extrusion are very suitable for polymers obtained in irregular particle form and with very low flowability, which therefore require pelletization in order to be transformed into a commercial product. However, at the present time, in the olefin polymerization field some catalysts and processes are becoming important which can produce regular shape polymer particles, in particular in spheroidal form, and having a controlled particle size distribution.

Said polymer particles, because of their high flowability, high bulk density values, and absence of fines, can be commercialized as produced without the necessity of transformation into extruded pellets. There is, therefore, a clear need for a process which will permit stabilization of the above mentioned particles as produced, without having to go through further extrusion and processing stages.

For this purpose some processes are employed whereby the polymer particles are treated with solutions or suspensions of stabilizers.

These processes, however, require additional steps to remove the solvent or the suspending medium, and have very little flexibility since they require a selection of solvents and/or treatment conditions which differ depending on the stabilizers used. Further they frequently do not provide a coating or surface treatment which survives storage intact and is effective after long periods of exposure to air, light and other elements.

FR-A-2 389 652 discloses a composition comprising a polyolefin, an organic phosphite stabilizer, a phenolic antioxidant and a benzotriazole light stabilizer. To prepare said composition the stabilizers can be mixed in the form of dry powders with the polymer, or dissolved in solvents and sprayed on the polymer particles, or can be mixed with the molten polymer in an extruder.

US-A-4,739,000 discloses a composition comprising a polyolefin, an organic phosphite stabilizer and a phenolic antioxidant, said stabilizers being mixed with the polymer by spraying a stabilizer solution on the polymer particles. In the Examples of this document, after the addition of stabilizers, the polymer is subjected to extrusion.

FR-A-2 301 558 discloses a composition comprising a polyolefin, an organic phosphite stabilizer and a phenolic antioxidant. Said composition is prepared by incorporating in the polymer the stabilizers in the solid state or in the form of a solution or dispersion, and is subsequently processed in a kneading machine or extruder.

US-A-4,377,651 discloses a polyolefin having incorporated therein a stabilizing system comprising a hindered amine and a metal phosphonate, and optionally a phenolic antioxidant and a phosphite stabilizer. The stabilizing system can be incorporated into the polymer by dry blending, or in the form of solutions or slurries, or mixed with the molten polymer in mixers, roll mills or extruders.

DE-A-22 60 213 deals with the problem of stabilizing polyolefins, by providing a product which is stable during storage or during a subsequent processing step, without the necessity for the stabilizers to be separately kneaded into the polymer. This document suggests the use of stabilizers selected among eight groups, such as for instance the group of substituted phenols and the group of organic phosphorus compounds. Moreover, this document teaches that addition of stabilizers in liquid state yields a poorer stability than is obtained with addition in the non liquid state, and that with the use of liquid stabilizers agglomeration of the polymer particles cannot be avoided; therefore, it is essential that the stabilizers are not in the liquid state; moreover, the contact between polymer and stabilizers must take place while the polymer temperature is higher than the melting temperature of the stabilizers.

This invention provides a process for preparing nonextruded stabilized olefin polymer particles, said process comprising the step of polymerizing an olefin monomer or olefin monomers in the presence of a Ziegler-Natta catalyst, thus obtaining directly olefin polymer particles having a spheroidal shape, and then the step of depositing a stabilizer mixture on the surface of said polymer particles, said stabilizer mixture being either a molten mixture or a mixture in which at least component (A) is in the liquid state, without containing any solvent, and comprising the following stabilizers (percent by weight with respect to the weight of the polymer particles):

A) from 0.02% to 0.15%, preferably from 0.03% to 0.01%, of one or more organic phosphites or phosphonites or mixtures thereof, which are liquid at room temperature or have a melting point below 100°C;

B) from 0.025% to 0.2%, preferably from 0.03% to 0.2%, most preferably from 0.04% to 0.1%, of one or more phenolic antioxidants with melting point from 45°C to 130°C; and, optionally, one or more of the following additional

components:

C) from 0.05 to 0.5%, preferably from 0.1% to 0.4%, of one or more thioethers or organic polysulfides or mixtures thereof;

D) from 0.1% to 1.0%, preferably from 0.15% to 0.8%, of one or more light stabilizers which are liquid at room temperature or have a melting point below 150°C, selected from the group consisting of hindered amine light stabilizers (HALS) and benzophenone and benzotriazole derivatives;

E) one or more diluents selected from the group consisting of paraffins and cycloparaffins which are liquid at room temperature, or have a melting point below 110°C, expoidized soy bean or linseed oil, silicone oils, and olefin oligomers in an amount not greater than 0.3%, preferably from 0.05% to 0.15%.

This process provides polyolefin particles which are stabilized against color changes and in general against oxidation and degradation phenomena caused by exposure to heat and light, especially in the presence of oxygen.

Moreover, with the present process the stabilizers can be deposited on the polymer particles as an almost continuous coating or at least a surface impregnation (depending on the composition of the liquid mixture and the porosity of the polymer particles being treated). The thus treated polymer particles have good resistance to storage for extended periods of time and to long periods of exposure to air and light.

The stabilizer mixture which is used according to the present invention is preferably selected in such a way that it remains in the liquid state at least at the temperature of the polymer particles as they come from the polymerization reactors (which usually not lower than 50-60°C and not higher than about 120°C), after the polymer separation and catalyst deactivation phases, so that it can, therefore, be added at this point in order to deposit an homogeneous coating on the surface of the particles themselves.

The percent by weight on the polymer expresses the concentration of each component (A), (B), (C), (D) and (E) with respect to the weight of the polymer particles on which they are deposited.

Given the small quantities of stabilizers which are deposited on the polymer particles according to the process of the present invention, it is possible to determine the respective proportions of the components in the mixture to be fed into the stabilization equipment (which will be described later on) directly on the basis of the above mentioned concentrations, without having to make corrections which would take into consideration the weight increase of the polymer after stabilization.

Therefore, one can use mixtures which include the single components in the following proportions (parts by weight):

- from 2 to 15 of (A);
- from 2.5 to 20 of (B);

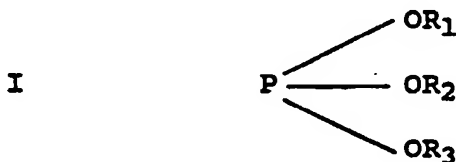
and optionally,

- from 5 to 50 of (C);
- from 10 to 100 of (D);
- up to 30 of (E);

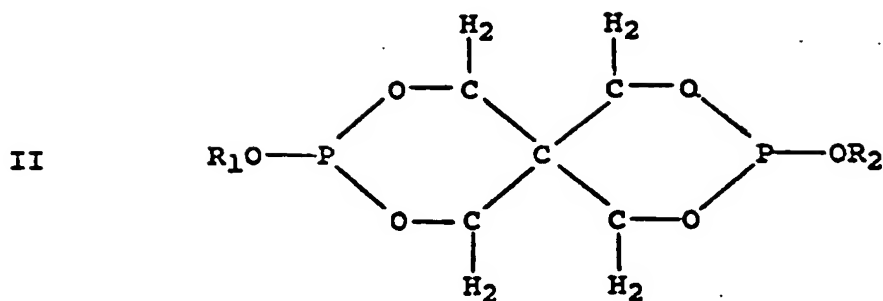
In order to compensate for any loss of stabilizers in the system, it is preferred to feed an excess of mixture, up to about 10%, with respect to the theoretical quantity, which is calculated on the basis of the weight of the polymer to be stabilized.

For instance, if one wants to stabilize 100 kg of polymer by depositing on the particles, by weight, 0.05% of (A) and 0.1% of (B), then 150 g of a liquid mixture containing 5 parts by weight of (A) and 10 parts of (B) will have to be fed, optionally adding a small excess of this mixture to compensate for system loss.

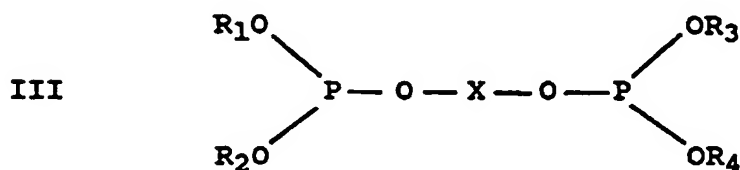
The organic phosphites which can be used as stabilizers according to the present invention are those compounds which are liquid at room temperature, or have a melting point below 100°C, including, preferably, those having the following general formulas:



where  $R_1$ ,  $R_2$  and  $R_3$  are the same or different and are  $C_{1-18}$  alkyl,  $C_{6-18}$  aryl, or  $C_{7-18}$  aralkyl radicals;



where  $R_1$  and  $R_2$  are the same or different and have the meaning indicated above;

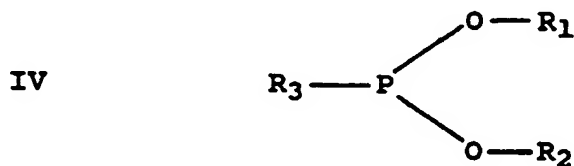


where  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are the same or different and have the same meaning as  $R_1$ ,  $R_2$  and  $R_3$  above, X is a bivalent  $C_{1-10}$  alkyl,  $C_{6-18}$  aryl or  $C_{7-20}$  aralkyl radical.

Specific examples of compounds, which are liquid or have a melting point below  $100^\circ\text{C}$ , included in the general formulas I, II, and III, are:

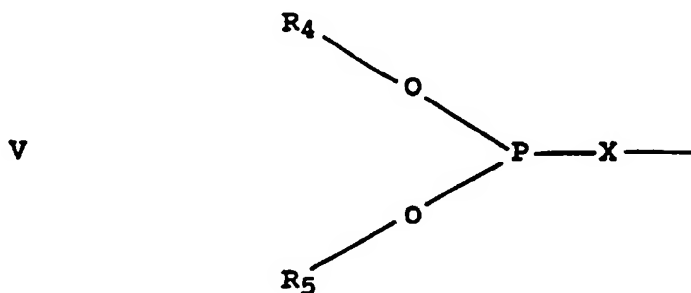
distearyl pentaerythrityl diphosphite, sold by BORG-WARNER CHEMICAL under the trademark Weston 618; 4,4'-butyldenebis(3-methyl-6-tert-butylphenyl-di-tridecyl)phosphite, sold by ADEKA ARGUS CHEMICAL under the trademark P; tris(monononyl phenyl) phosphite.

The organic phosphonites which are liquid at room temperature or have a melting point below  $100^\circ\text{C}$ , include, preferably, those having the following general formula:



where  $R_1$ ,  $R_2$ , and  $R_3$  are the same or different and are  $C_{1-18}$  alkyl,  $C_{6-18}$  aryl, or  $C_{7-18}$  aralkyl radicals.

Alternatively, and this is a further preferred case, the  $R_3$  radical can be the group



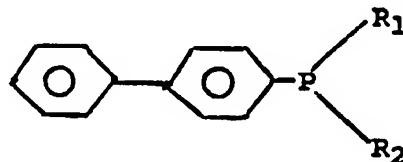
where  $R_4$  and  $R_5$  are the same or different and have the same meaning as set forth above for  $R_1$  and  $R_2$ , and X is a

EP 0 411 628 B1

bivalent  $C_{1-10}$  alkyl,  $C_{6-18}$  aryl, or  $C_{7-20}$  aralkyl radical.

Specific examples of phosphonites which are liquid at room temperature or have a melting point below  $100^{\circ}\text{C}$ , included in the general formulas IV and V, are the compounds having the following formulas:

VI



where  $R_1$  and  $R_2$  are both  $-\text{O}-\text{C}_4\text{H}_9$ ,  $-\text{O}-\text{C}_8\text{H}_{17}(\text{iso})$  or

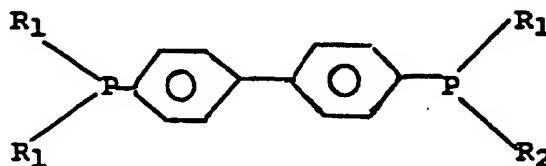


radicals, or either  $R_1$  or  $R_2$  group is a

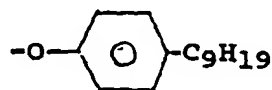
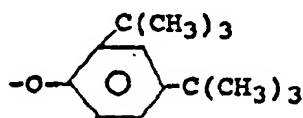


radical, while the other is a  $-\text{O}-\text{C}_4\text{H}_9$  or  $-\text{O}-\text{C}_8\text{H}_{17}(\text{iso})$  radical;

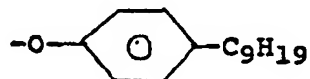
VII



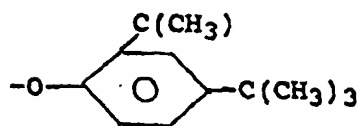
where  $R_1$  and  $R_2$  are both  $-\text{O}-\text{C}_4\text{H}_9$ ,  $-\text{O}-\text{C}_8\text{H}_{17}(\text{iso})$ ,



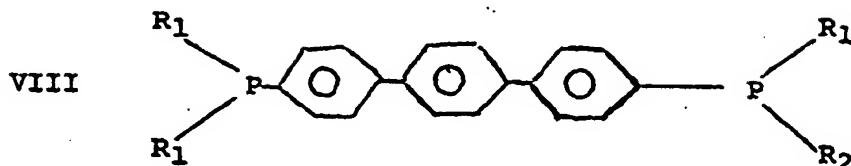
radicals or  $R_1$  is a



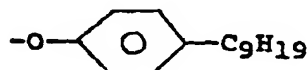
radical and  $R_2$  is a  $-\text{O}-\text{C}_8\text{H}_{17}$ ,  $-\text{O}-\text{C}_8\text{H}_{17}(\text{iso})$ , or  $-\text{O}-\text{C}_4\text{H}_9$  radical, or  $R_1$  is a



radical and  $R_2$  is a  $-O-C_4H_9$  radical;



where  $R_1$  and  $R_2$  are both  $-O-C_8H_{17}$  or



radicals, or  $R_1$  is a

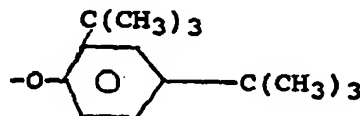


radical and  $R_2$  is a



radical.

Most preferred is the compound of the formula VII where  $R_1$  and  $R_2$  are both



radicals.

Said compound, the chemical name of which is tetrakis(2,4-di-tert-butylphenyl)4,4'-biphenylene diphosphonite, is the main component of a stabilizing composition sold by Sandoz under the Sandostab P-EPQ trademark.

As stated above, the stabilizing mixtures of the present invention also comprise one or more phenolic antioxidants, i.e. sterically hindered phenols having a 45° to 130°C melting point.

Examples of preferred phenolic antioxidants are:

2,6-di-tert-butyl-4-methylphenol, sold by Shell under the Ionol trade-mark; 2,2-bis(4-(2-(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyloxy))ethoxyphenyl)propane, sold by ICI under the Topanol 205 trademark; octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, sold by Ciba Geigy under the Irganox 1076 trade-mark; and pentaerythritol tetrakis 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate, sold by Ciba Geigy under the Irganox 1010 trade-mark.

Examples of thioethers which can be used as additional component (C) are dilauryl thiodipropionate and distearyl thiodipropionate.

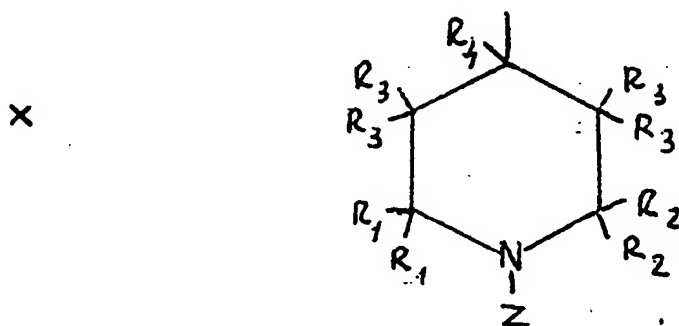
Preferred examples of organic polysulphides are the compounds with the following general formula:



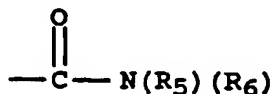
where the R radicals are the same or different and are  $\text{C}_{1-20}$  alkyl,  $\text{C}_{6-20}$  aryl, or  $\text{C}_{7-20}$  aralkyl radicals.

Particularly preferred is the compound of formula IX where R is a  $-\text{C}_{18}\text{H}_{37}$  radical, sold by Hoechst under the HOSTANOX SE 10 trademark.

The HALS which can be used as additional components (D) are compounds which are liquid at room temperature or have a melting point below  $130^\circ\text{C}$ , and include, in the molecule, one or more substituted piperidyl groups with the following general formula:



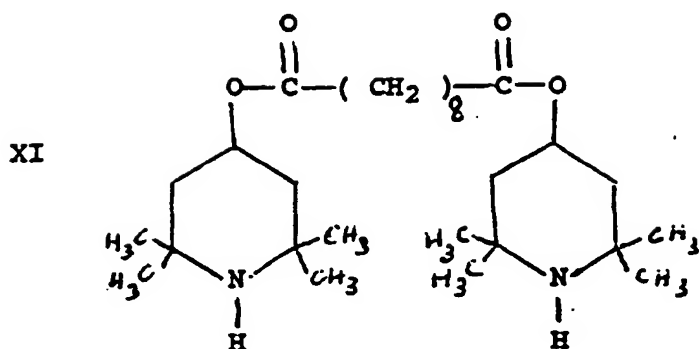
where the  $\text{R}_1$  radicals are the same or different and are  $\text{C}_1\text{-C}_4$  alkyl radicals, tetramethylpiperidyl radicals, or the alkyl radicals form, together with the piperidyl carbon atoms to which they are bonded, a  $\text{C}_5\text{-C}_9$  cycloalkyl radical; the  $\text{R}_2$  radicals are the same or different and are hydrogen or  $\text{C}_1\text{-C}_{18}$  alkyl radicals,  $\text{C}_7\text{-C}_{18}$  aralkyl radicals, or the alkyl radicals form, together with the piperidyl carbon atoms to which they are linked, a  $\text{C}_5\text{-C}_{10}$  cycloalkyl radical; the  $\text{R}_3$  radicals are the same or different and are hydrogen, or  $\text{C}_1\text{-C}_{18}$  alkyl radicals or  $\text{C}_7\text{-C}_{18}$  aralkyl radicals; the  $\text{R}_4$  radical is hydrogen, a  $\text{C}_1\text{-C}_8$  alkyl radical or a benzyl radical; Z is hydrogen, or a  $\text{C}_1\text{-C}_{18}$  alkyl radical, or a  $\text{C}_1\text{-C}_{12}$  alkylene,  $\text{C}_3\text{-C}_{12}$  alkenyl,  $\text{C}_3\text{-C}_5$  alkynyl,  $\text{C}_7\text{-C}_{18}$  aralkyl,  $\text{C}_2\text{-C}_4$  acyl,  $\text{C}_2\text{-C}_{18}$  alkanoyl,  $\text{C}_3\text{-C}_{18}$  alkoxyalkyl,  $\text{C}_3\text{-C}_{18}$  alkenoyl, oxyl, cyanomethyl, xylilene radical, or a radical with a valence from 1 to 4 and containing from 1 to 4 hydroxyl groups and, optionally, ether, ester or N, S or O containing heterocyclic group, wherein the radical has the valences linked to nitrogen of the piperidyl groups, or a bivalent radical containing one or more ester or amide groups, or a



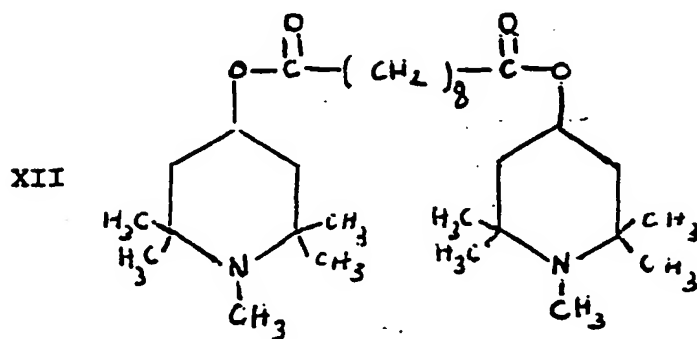
radical where  $\text{R}_5$  and  $\text{R}_6$  are hydrocarbon radicals.

Preferably Z is a  $\text{C}_1\text{-C}_{12}$  alkyl radical, or a  $\text{C}_3\text{-C}_8$  alkenyl,  $\text{C}_7\text{-C}_{11}$  aralkyl radical, or a bivalent radical containing one or more ester groups, said bivalent radical having valences linked to the nitrogen of the piperidyl groups.

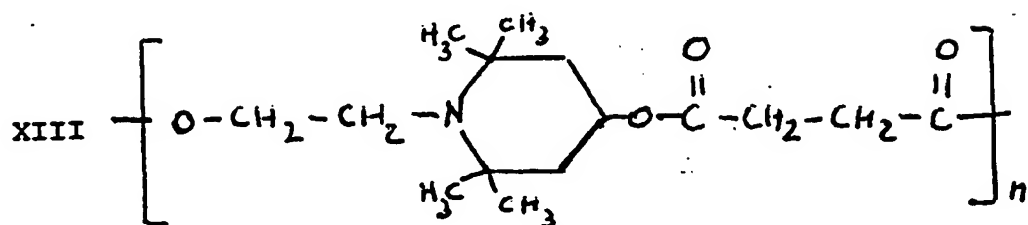
Preferred examples of HALS which are liquid or have a melting point below  $130^\circ\text{C}$  are the compounds having the following formulas:



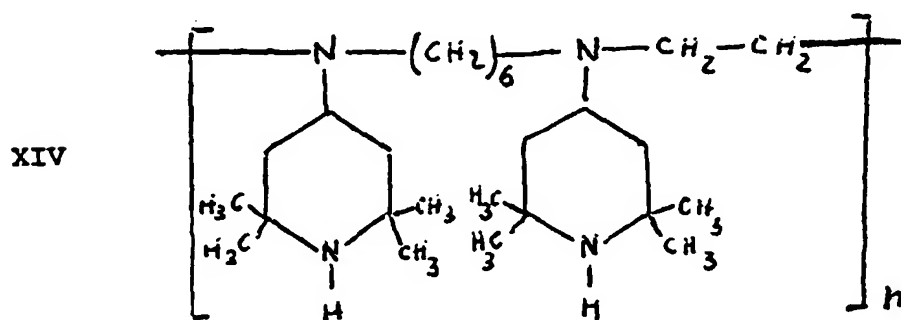
sold by CIBA-GEIGY under the Tinuvin 770 trade-mark



sold by CIBA-GEIGY under the Tinuvin 292 trade-mark

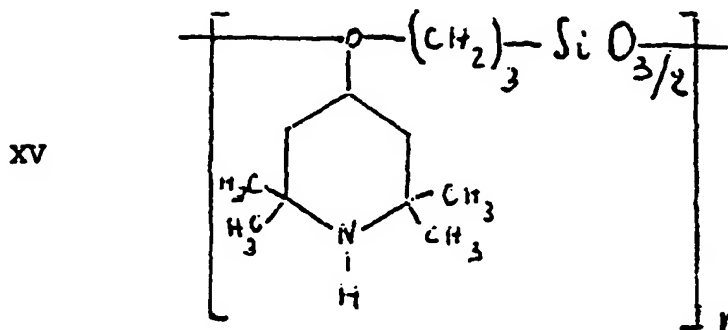


where n is from 2 to 10. A compound of this type is sold by CIBA-GEIGY under the Tinuvin 622 trade-mark.





where n is from 2 to 100. A compound of this type is sold by Montedison under the SPINUVEX A-36 trade-mark.



where n is from 2 to 100. A compound of this type is sold by Enichem under the Uvasil 299 trade-mark.

Preferred examples of benzophenone or benzotriazole derivatives are: 2-hydroxy-4-octyloxybenzophenone, sold by Ciba-Geigy under the Chimassorb 81 trade-mark; and 2-(2'-hydroxy-3-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, sold by Ciba-Geigy under the tinuvin 326 trade-mark.

Examples of diluents (E), besides the epoxidized soy bean or linseed oils, are the microcrystalline paraffin waxes having a melting point from 60° to 90°C, and preferably a penetration point between 20 to 90, most preferably between 30 and 80, at 25°C (5 seconds/100 g, DIN 51579, ASTM D 1321). Products of this type are sold by WITCO CHEMICAL under the MULTIWAX trade-mark.

Examples of silicone oils and olefin oligomers are the BAYSILONE M 100 silicone oil of BAYER, H-300 polybutene of AMOCO, NAPVIS D 03, D 07 and D10 of BRITISH PETROLEUM.

Among the liquid mixtures having the compositions described above, particularly preferred are those comprising:

A) tetrakis(2,4-di-tert-butylphenyl)4,4'-biphenylene diphosphonite;

B) pentaerythrityl-tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate) and optionally octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate,

and optionally,

D) the HALS of formula XII;

E) one or more of the diluents described above, in the proportions required by the present invention.

The above mentioned mixtures are liquid even at room temperature.

As previously mentioned, the present liquid stabilizer mixtures are deposited on the surface of the polymer particles after discharge from the polymerization reactor, separation of the polymer, deactivation of the catalyst and purification phases.

Said phases include the removal, e.g. through "flashdrying", of the excess liquid monomer or solvent that may be present in the polymerization reactor discharge (separation), and the deactivation (killing) of the catalyst. Volatile substances, such as solvents, unreacted monomers and oligomers, if any, can be removed during the deactivation phase.

The latter can be done by treating the polymer particles with inert gases, (nitrogen, for example) at high temperatures (up to a few degrees below the polymer melting point), and/or steam. Preferably pure steam or steam diluted with nitrogen is used.

Whenever steam is used, there can be an additional drying stage, with nitrogen or other inert gases, for example, in order to eliminate the residual moisture from the polymer particles.

Upon exiting the separation and deactivation systems, the polymer particles usually have a temperature not lower than 50°C, more typically not lower than 60°C. It is preferred to deposit the liquid stabilizer mixture described previously on said particles while the particles still hot, using known methods of surface addition, for example, by using continuous or discontinuous mixers (particularly horizontal mixers) optionally equipped with a spraying mechanism.

It is desirable that the residence time of the polymer particles in the mixer be at least 5 minutes, in order to obtain a good distribution of the stabilizing mixture on the surface of the particles.

The molten or liquid stabilizer mixture can be prepared and preserved in a vessel provided with a heating jacket and a mechanical agitator, introducing the components of the mixture in increasing melting point order.

Usually the operation occurs in a nitrogen atmosphere at temperatures between 90°C and 140°C, and the molten

or liquid mixture is sent to the additivition plant section through pumps and feeders.

Downstream from the stabilization described above, or within the same plant section used for it, before or after the addition of the molten or liquid stabilizer mixture, other stabilizers and additives can be used, such as HALS with a melting point higher than 150°C, metal stearates (Ca and Na stearates for example), synthetic hydrotalcite, glyceryl monostearate, slip agents (such as erucamide, oleamide), antiblocking agents (like SiO<sub>2</sub> or synthetic zeolites), nucleating agents, antistatic agents, etc.

If the addition of the above mentioned stabilizers and additives is done after the molten or liquid mixture has been deposited according to the present invention, it is desirable to select the composition of the liquid or molten stabilizer mixture and the operating conditions in such a way that the mixture of stabilizers on the particles is maintained fluid at least during the introduction of the additional additives and solid stabilizers, thus allowing them to adhere to the polymer particles.

The polyolefins which can be conveniently stabilized through the process of the present invention include polymers and copolymers, or their mixtures obtained through sequential polymerization, of olefins of formula R-RC=CH<sub>2</sub>, where R is a hydrogen atom, or an alkyl radical with 1-6 carbon atoms or a C<sub>6-12</sub> aryl.

In particular, said polyolefins comprise:

- 1) isotactic or mainly isotactic polypropylene;
- 2) HPPE (i.e. ethylene copolymers having usually a density of 0.95 g/cm<sup>3</sup> or greater), LLDPE (i.e. ethylene homopolymers having usually a density of 0.91 g/cm<sup>3</sup> or greater), LDPE (i.e. ethylene homopolymers having usually a density of 0.91 g/cm<sup>3</sup> or greater)
- 3) crystalline copolymers of propylene with ethylene and/or other C<sub>3-8</sub> straight or branched alpha-olefins such as 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene;
- 4) ethylene/C<sub>3-8</sub> alpha-olefin elastomeric copolymers and ethylene/C<sub>3-8</sub> straight or branched alpha-olefin/diene terpolymers containing minor portions of diene, where the alpha-olefin is straight or branched and preferably selected among propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-butene and is present in an amount of 30 to 80 wt.%;
- 5) heterophasic polymers obtained through sequential polymerization, comprising (A) a propylene homopolymer fraction or one of the copolymers mentioned in item (3), above, and a copolymer fraction (B) of an elastomeric copolymer mentioned in item (4) above (typically the copolymer fraction (B) is present in an amount from 10 to 60 wt. %).

Examples of dienes which are most commonly present in the above mentioned elastomeric copolymers are the butadiene, the ethylidene-norbornene, and the 1-4 hexadiene (typically the diene is present in an amount from 1 to 10 wt. %).

The olefin polymers can be synthesized with any Ziegler-Natta catalyst which can produce polymer particles with a spheroidal geometrical shape, such as to guarantee good flowability. The preferred flowability values are between 9 and 16 seconds, measured according to ASTM norm 1895-69 method A.

It is also desirable that the polymer particles have a bulk density between 0.3 and 0.6 g/cm<sup>3</sup>, determined according to ASTM norm 1895-69 method A.

Specific examples of catalysts which can be used for the preparation of polyolefins in particulate form with the above mentioned characteristics, are the nonsupported Ziegler-Natta catalysts obtained from (A) a solid component made up of particles of TiCl<sub>3</sub> derived by reducing TiCl<sub>4</sub> with organic aluminum compounds, with (B) an aluminum alkyl compound, such as diethylaluminum chloride.

Other examples are the supported Ziegler-Natta catalysts, obtained by the reaction of a solid component comprising a Ti compound with at least one Ti-Cl link, and, optionally, an electron-donor compound supported on MgCl<sub>2</sub> in particles of a regular, essentially symmetrical, usually spheroidal geometrical form, with an organic aluminum compound, particularly a trialkyl aluminum compound, optionally combined with an electron-donor compound.

Among the supported catalysts, those containing MgCl<sub>2</sub> in active form are preferred, i.e. those which are characterized by an X-ray spectrum where the maximum intensity reflection which appears in the spectrum of a normal magnesium chloride is substituted by a halo with maximum intensity moved over with respect to the maximum intensity reflection, or by the fact that said reflection shows an enlargement.

The catalyst component supported on MgCl<sub>2</sub> in particles of the aforementioned regular geometrical form can be obtained through various methods.

For examples, it is possible to prepare spherical particles of MgCl<sub>2</sub> adducts with electron-donor compounds preferably containing active hydrogen atoms, such as H<sub>2</sub>O, alcohols, phenols, and treat said spherical particles with the Ti compound, and optionally with an electron-donor compound. Before the reaction with the titanium compound, the electron-donor compound present in the adduct with the magnesium chloride can be at least partially removed from the adduct itself, for example by thermal treatment or by reaction with alkyl aluminum compounds.

## EP 0 411 628 B1

Examples of preparation methods of catalyst components of this type are described in US -A- 3,953,414 and 4,399,054.

Another example for the preparation of catalyst components supported on  $MgCl_2$  in particles of said regular geometrical form, include the reaction of a Ti compound with spheroidal particles comprising an alcoholate or halogenoalcoholate of Mg or their mixtures. Specific methods for the preparation of catalytic components of this type are described in US -A- 4,220,554.

Examples of highly active and stereospecific catalysts, that can be obtained by reaction of the above mentioned catalyst components with an aluminum alkyl compound and an electron-donor compound selected among specific silanes classes, are described in EP-B- 45,977, and in EP-A- 45,976 and 45,975.

Alternately, the catalyst component containing the Ti compound can be deposited on an inert support of a regular form and organic nature (for example styrene polymers) or inorganic nature (microspheroidal silica, for instance).

Examples of this type of catalysts are shown in EP-A- 283,011 and 344,755.

Other examples of supported Ziegler-Natta catalysts capable of producing polyolefin particles of said regular geometrical shape are described in EP-A- 250,230 and 216,402.

The catalysts described above are, among other things, capable of producing polyolefin particles having a controlled particle size (i.e., without extremely fine powders or excessively large particles), and, therefore, they are particularly suited for stabilization with the process of the present invention.

A preferred example of particles which are particularly suited for stabilization with the present process are spherical or spheroidal particles having a diameter from 0.5 to 4.5 mm and a controlled particle size distribution, i.e. with at least 90% of the particles having a diameter between 0.5 and 3.5 mm.

The polyolefins in particle form having said regular geometrical shape are prepared according to known polymerization processes, operating in liquid phase, for instance, in the presence or absence of an inert hydrocarbon solvent, or in gas phase, or even combining liquid and gas phase polymerization stages.

The polymerization temperature is generally between 40°C and 160°C, and the process is carried out at atmospheric pressure or higher.

The polymers stabilized with the present process, i.e. in form of nonextruded particles having said spheroidal shape, coated or impregnated at least on the surface with the stabilizers and additional components described above can be used directly for the transformation into finished products.

Following are examples which are illustrative of the process of this invention, the products produced and the physical properties thereof.

In the following examples two types of spherical polymers were used:

a) spherical polypropylene homopolymer (MIL = 1.5) with the following particle size distribution:

$\varnothing > 3.5 \text{ mm} = 1\%$        $\varnothing = \text{diameter}$

$2 < \varnothing < 3.5 \text{ mm} = 48\%$

$1 < \varnothing < 2 \text{ mm} = 49\%$

$0.5 < \varnothing < 1 \text{ mm} = 2\%$

- fraction insoluble in boiling n-heptane = 97% by weight
- bulk density = 0.49 Kg/l
- flowability = 13 sec.

b) propylene/ethylene heterophasic spherical composition containing 14% by weight of ethylene, said composition being formed by polypropylene homopolymer and elastomeric ethylene-propylene copolymer, with the following particle size distribution:

$\varnothing > 3.5 \text{ mm} = 2\%$

$2 < \varnothing < 3.5 \text{ mm} = 54\%$

$1 < \varnothing < 2 \text{ mm} = 42\%$

$0.5 < \varnothing < 1 \text{ mm} = 2\%$

- bulk density = 0.50 kg/l
- flowability = 14 sec.

### EXAMPLE 1

In a 1 litre spherical glass flask were introduced:

- IRGANOX 1010      g 100

## EP 0 411 628 B1

- SANDOSTAB-P-EPQ g 50
- ROL/OB 55-AT paraffin oil (\*) g 100  
(\*) paraffin oil having a density of 0.885 + 10% kg/l at 15°C (ASTM D 1298)

5 and flowing point (ASTM D 97) = -10 + 2 °C.

The ingredients were heated to 120°C, under agitation and in N<sub>2</sub> atmosphere, until a homogeneous liquid was obtained.

In a 14 litre Henschel mixer were introduced 2 Kg of spherical particles of polypropylene which were heated to 65°-70°C, together with 1 g of glyceryl monostearate.

10 On the hot polypropylene particles were fed 5 g of the liquid stabilizer mixture and the particles and the liquid were mixed at 1500 rpm for about 5 minutes.

1 g of Ca-stearate was then added to the mixer and the contents were stirred again for 1-2 minutes. The stabilized spherical polypropylene was then discharged.

15 The "pepper-salt" test, carried out in a 150°C oven on the stabilized spherical polypropylene, showed the first oxidized particles (i.e., yellowing particles) after about 20 hours.

The same spherical polymer, without any stabilization treatment, when submitted to the same test, was completely yellow after 2 hours.

20 The thermal oxidation test carried out on pressure-injected plaques 2 mm thick obtained from the above mentioned stabilized polymer, showed a resistance of 30 days in a 150°C oven. The test was considered completed when the first signs of cracking appeared on the sample.

### EXAMPLE 2

25 Using the same method and ingredients of example 1, a stabilizing liquid mixture was prepared which was constituted by:

- IRGANOX 1010 g 100
- IRGANOX 1076 g 50
- SANDOSTAB-PEPQ g 100
- 30 - ROL/OB 55 A-T paraffin oil g 100

4.5 g of which were fed on 2 kg of said spherical polypropylene following the same method as in example 1.

35 After the addition and mixing was complete, 1 g of Ca-stearate was added and mixed. The stabilized spherical polypropylene was then discharged. The following test results were obtained:

"pepper-salt" 150°C = 16 hours  
thermal oxidation 150° = 13 days

### EXAMPLE 3

40 Using the same method and ingredients of example 1 a liquid stabilizing mixture was prepared made up of:

- IRGANOX 1010 g 100
- IRGANOX 1076 g 50
- 45 - SANDOSTAB-PEPQ g 100

2.5 g of which were fed on 2 kg of said spherical polypropylene in the same way as described in example 1.

After the addition of 1 g of Na-stearate the stabilized spherical polypropylene was discharged.

50 The following test results were obtained:

"pepper-salt" 150°C = 14 hours  
thermal oxidation 150°C = 12 days

### EXAMPLE 4

55 Using the same method and ingredients of example 1 a liquid stabilizing mixture was prepared made up of:

- IRGANOX 1010 g 100

## EP 0 411 628 B1

- SANDOSTAB-PEPQ g 100
- epoxidized linseed oil g 100

3 g of which were fed on 2 Kg of said spherical polypropylene in the same way as described in example 1.

5 The stabilized spherical polypropylene was discharged and the following test results were obtained:

"pepper-salt" 150°C = 12 hours  
thermal oxidation 150° = 14 days.

### 10 EXAMPLE 5

Using the same method and ingredients of example 1 a liquid stabilizing mixture was prepared made up of:

- IRGANOX 1010 g 100
- 15 - SANDOSTAB-PEPQ g 50
- DSTDP = distearyl thiodipropionate g 100

7 g of which were fed on 2 Kg of said spherical polypropylene in the same way as described in example 1.

20 After the addition of 1 g of Ca-stearate, the stabilized spherical polypropylene was discharged and the following test results were obtained:

"pepper-salt" 150°C = 8 hours  
thermal oxidation 150° = 50 days.

### 25 EXAMPLE 6

Using the same method and ingredients of example 1 a liquid stabilizing mixture was prepared made up of:

- IRGANOX 1010 g 100
- 30 - IRGANOX 1076 g 50
- SANDOSTAB-P-EPQ g 100
- Carlo Erba paraffin wax MP=70°C g 100  
(MP - melting point)

35 7 g of which were fed on 2 Kg of said spherical polypropylene in the same way as described in example 1.

After the addition of 1 g of synthetic hydrotalcite (SHT), the stabilized spherical polypropylene was discharged and following test results were obtained:

40 "pepper-salt" 150°C = 24 hours  
thermal oxidation 150° = 35 days.

### EXAMPLE 7

With the same method described in example 1 a liquid stabilizing mixture was prepared made up of:

- 45 - IRGANOX 1010 g 100
- IRGANOX 1076 g 50
- SANDOSTAB-P-EPQ g 100
- WITCO microcrystalline paraffin wax g 100  
50 MP = 77°C (MULTIWAX W-835)

3.5 g of which were fed on 2 Kg of spherical polypropylene in the same way as described in example 1.

After the addition of 1 g of Ca-stearate, the stabilized spherical polypropylene was discharged and the following test results were obtained:

55 "pepper-salt" 150°C = 18 hours  
thermal oxidation 150° = 12 days.

**EXAMPLE 8**

Using the same method and ingredients of example 1 a liquid stabilizing mixture was prepared made up of:

- 5 - IRGANOX 1010 g 50
- SANDOSTAB-P-EPQ g 50
- TINUVIN 292 g 450

10 11 g of which were fed on 2 Kg of spherical heterophasic propylene-ethylene composition following the same procedure described in example 1.

Then 10.3 g gray pigment (containing  $\text{TiO}_2$  and carbon black) and 1 g of Ca-stearate were added to the mixer, mixing for 2 more minutes at 1500 rpm.

15 Plaques (3 mm thick) of the stabilized heterophasic spherical composition were obtained, through pressure injection at 230°C, and submitted to accelerated U.V. resistance tests by using a XENOTEST 1200 under the following conditions:

- black panel temperature 63°C
- relative humidity 60%
- machine room temperature = about 43°C
- 20 - dry/wet cycle 102/18 min
- light/light cycle (continuous irradiation)

25 The evaluation of the surface deterioration of the sample was done in terms of color variation (whitening) by increasing the L colorimetric coordinate (correct luminosity) determined with a GARDNER HUNTERLAB tristimulus colorimeter model 25-9.

The sample stabilized with the liquid mixture described above showed an L of two units after being exposed for 1200 hours,

A sample stabilized with the same formulation omitting the TINUVIN 292 shows an L of 5 units after only 350 hours.

30 **EXAMPLE 9**

Using the same method and ingredients of example 1 a liquid stabilizing mixture was prepared made up of:

- IRGANOX 1010 g 50
- 35 - IRGANOX 1076 g 25
- SANDOSTAB-P-EPQ g 50
- TINUVIN 770 g 450
- WITCO microcrystalline paraffin g 100
- wax MP = 77°C (MULTIWAX W-835)

40 13.5 g of which were fed on 2 Kg of spherical heterophasic propylene-ethylene composition in the same way as in example 1.

In the mixer were then added 10.3 of gray pigment and 1 g of Ca-stearate, mixing for 2 more minutes at 1500 rpm.

45 From the stabilized heterophasic spherical composition were prepared 3 mm thick plaques, by pressure injection at 230°C, which were submitted to accelerated UV resistance tests in the same apparatus and same operating conditions described in example 8.

The samples showed an increment in L values equal to 1.8 units after an exposure of 1200 hours.

50 **EXAMPLE 10**

In an 8 litre stainless steel autoclave, equipped with a mechanical agitator, heating jacket fed with steam at 120°C, and an inert gas blanket, are introduced, in order and at intervals of about 15 minutes:

- ROL OB/55-AT paraffin oil Kg 1
- 55 - IRGANOX 1076 Kg 0.5
- SANDOSTAB-P-EPQ Kg 2
- IRGANOX 1010 Kg 1

maintaining the agitation for at least 1 hour after the introduction of the last component.

In a 130 litre discontinuous Lodige horizontal mixer, were introduced 30 Kg of spherical polypropylene and 15 g of glyceryl monostearate heated, under agitation, to 70°C by introducing steam in the heating jacket.

With continuous agitation, 67.5 g of the liquid stabilizing mixture taken from the autoclave were added, and agitation was continued for about 5 minutes at about 79 rpm.

15 g of Ca-stearate were then added to the mixer, the contents were blended for further 1-2 minutes and then discharged.

The stabilized product showed the following test results:

- "pepper-salt" 150°C = 18 hours
- thermal oxidation 150°C = 14 days.

## Claims

1. A process for preparing nonextruded stabilized olefin polymer particles, said process comprising the step of polymerizing an olefin monomer or olefin monomers in the presence of a Ziegler-Natta catalyst, thus obtaining directly olefin polymer particles having a spheroidal shape, and then the step of depositing a stabilizer mixture on the surface of said polymer particles, said stabilizer mixture being either a molten mixture or a mixture in which at least component (A) is in the liquid state, without containing any solvent, and comprising the following stabilizers (percent by weight with respect to the weight of the polymer particles):

A) from 0.02% to 0.15% of one or more organic phosphites or phosphonites or mixtures thereof which are liquid at room temperature or have melting point below 100°C;

B) from 0.025 to 0.2% of one or more phenolic antioxidants with melting point from 45° to 130°C;

and, optionally, one or more of the following additional components:

C) from 0.05% to 0.5% of one or more thioethers or organic polysulfides or mixtures thereof;

D) from 0.1% to 1.0% of one or more light stabilizers which are liquid at room temperature or have a melting point below 150°C, selected from the group consisting of hindered amine light stabilizers, benzophenone and benzotriazole derivatives;

E) one or more diluents selected from the group consisting of paraffins and cycloparaffins which are liquid at room temperature or have a melting point below 110°C, epoxidized soy bean or linseed oil, silicone oils and olefin oligomers in an amount not greater than 0.3%.

2. The process of claim 1, wherein the olefin polymers are selected from the group consisting of:

1) isotactic or mainly isotactic polypropylene;

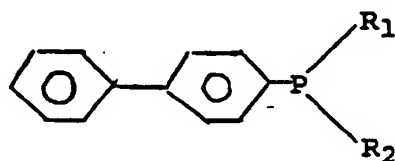
2) HDPE, LLDPE, LDPE polyethylene

3) crystalline copolymers of propylene with ethylene and/or other C<sub>3-8</sub> straight or branched alpha-olefins;

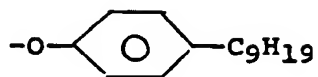
4) elastomeric ethylene/C<sub>3-8</sub> alpha-olefin copolymers and elastomeric ethylene/C<sub>3-8</sub> alpha-olefin/diene terpolymers containing minor proportions of diene, where the alpha-olefin is selected among propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-butene;

5) heterophasic polymers comprising (A) a homopolymer fraction of the propylene or one of the copolymers defined in item (3) and a copolymer fraction (B) of the elastomeric copolymers defined in item (4).

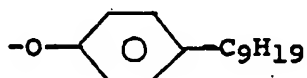
3. The process of claim 1, wherein the stabilizers (A) are selected from the group consisting of distearyl/pentaerythrityl diphosphite; 4,4'-butylidene bis (3-methyl-6-tert-butylphenyl-di-tridecyl) phosphite; tri(monononylphenyl) phosphite, and compounds having the following formulas:



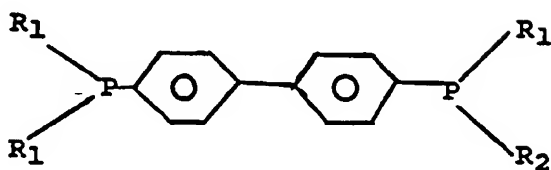
where  $R_1$  and  $R_2$  are both  $-O-C_4H_9$ ,  $-O-C_8H_{17}(\text{iso})$  or



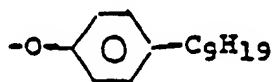
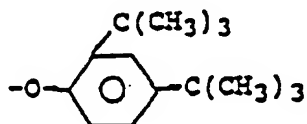
radicals, or one of the two  $R_1$  and  $R_2$  groups is a



radical, while the other is a  $-O-C_4H_9$  or  $-O-C_8H_{17}(\text{iso})$  radical;



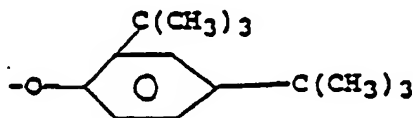
where  $R_1$  and  $R_2$  are both  $-O-C_4H_9$ ,  $-O-C_8H_{17}(\text{iso})$ ,



radicals or  $R_1$  is a

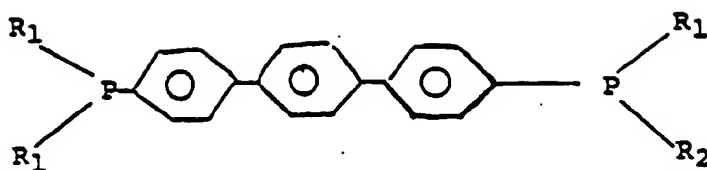


radical and  $R_2$  is a  $-O-C_8H_{17}$ ,  $-O-C_8H_{17}(\text{iso})$ , or  $-O-C_4H_9$  radical, or  $R_1$  is a

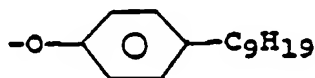


radical and  $R_2$  is a  $-O-C_4H_9$  radical;





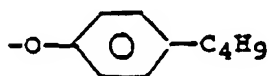
where R<sub>1</sub> and R<sub>2</sub> are both -O-C<sub>8</sub>H<sub>17</sub> or



radicals, or R<sub>1</sub> is a



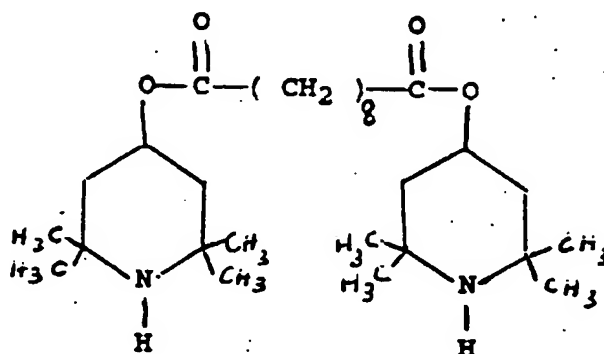
radical and R<sub>2</sub> is a



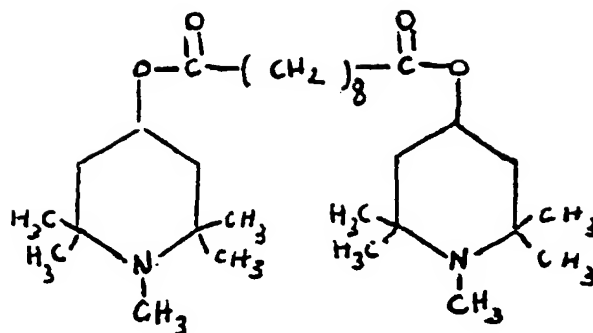
radical.

4. The process of claim 1, wherein the stabilizers (B) are selected from the group consisting of 2,6-di-tert-butyl-4-methylphenol, 2,2-bis(4-(2-(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyloxy))ethoxyphenyl)propane, and octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate.
5. The process of claim 1, wherein components (C) are selected from the group consisting of dilauryl thiodipropionate; distearyl thiodipropionate and compounds having the general formula (IX) R S S R, where the R radicals, the same or different, are alkyl, aryl or aralkyl radicals with 1 to 20 carbon atoms.
6. The process of claim 1, wherein the light stabilizers (D) are selected from the group consisting of compounds having the formulas:

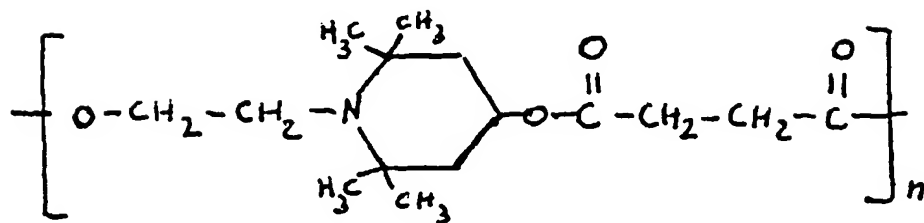
XI



XII

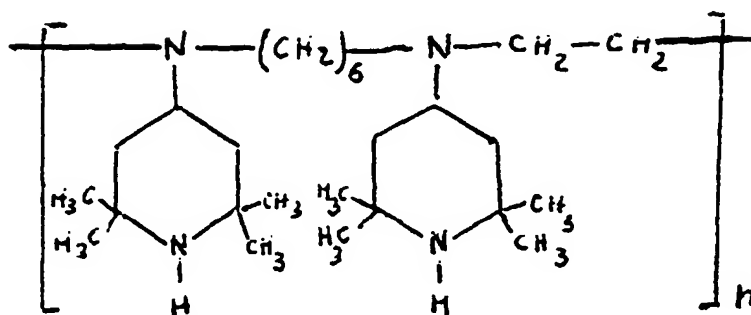


XIII

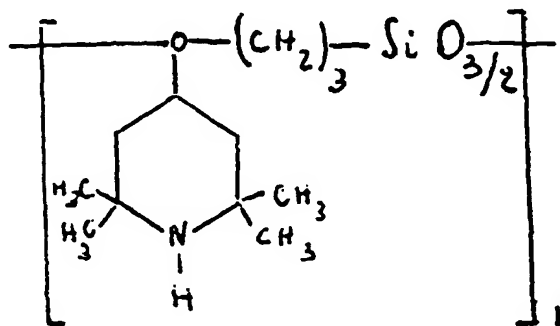


where n is from 2 to 10,

XIV



XV



where n is from 2 to 100, 2-hydroxy-4-n-octyloxy benzophenone and 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole.

7. The process of claim 1, wherein as diluent (E) are used microcrystalline paraffin waxes having a melting point from 60°C to 90°C.

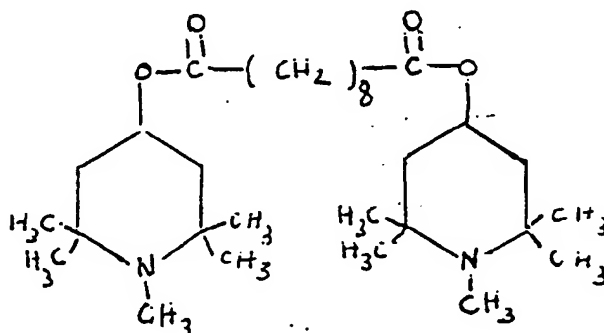
8. The process of claim 1, wherein the liquid mixture comprises the following stabilizers:

A) tetrakis(2,4-di-tert-butylphenyl)4,4'-diphenylene diphosphonite;

B) pentaerythrityl tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate) and optionally octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate,

and optionally,

D) the hindered amine light stabilizer of formula XII,



and  
E) one or more diluents.

9. The process of claim 1, wherein the liquid mixture is deposited on the polymer particles having a temperature not lower than 50°C.

## Patentansprüche

1. Verfahren zur Herstellung von nichtextrudierten stabilisierten Olefinpolymerteilchen, wobei dieses Verfahren umfaßt: die Stufe einer Polymerisation eines Olefinmonomeren oder mehrerer Olefinmonomeren in Anwesenheit eines Ziegler-Natta-Katalysators, wobei man direkt Olefinpolymerteilchen mit einer sphäroidalen Form erhält, und anschließend die Stufe einer Abscheidung einer Stabilisatormischung auf der Oberfläche dieser Polymerteilchen, wobei diese Stabilisatormischung entweder eine geschmolzene Mischung ist oder eine Mischung, in der sich zumindest Komponente (A) in flüssigem Zustand befindet, ohne daß irgendein Lösungsmittel enthalten ist, und die folgenden Stabilisatoren (Gew.-% in bezug auf das Gewicht der Polymerteilchen) umfaßt:

A) von 0,02 bis 0,15% eines oder mehrerer organischer Phosphite oder Phosphonite oder Mischungen hiervon, die bei Raumtemperatur flüssig sind oder einen Schmelzpunkt unterhalb 100 °C besitzen;

B) von 0,025 bis 0,2% eines oder mehrerer phenolischer Antioxidantien mit einem Schmelzpunkt von 45 bis 130 °C;

und gegebenenfalls eine oder mehrere der folgenden weiteren Komponenten:

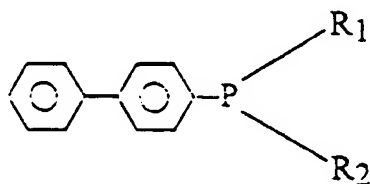
C) von 0,05 bis 0,5% eines oder mehrerer Thioether oder organischer Polysulfide oder Mischungen hiervon;  
D) von 0,1 bis 1,0% eines oder mehrerer Lichtstabilisatoren, die bei Raumtemperatur flüssig sind oder einen Schmelzpunkt unterhalb 150 °C besitzen, ausgewählt aus der Gruppe der gehinderten Amin-Lichtstabilisatoren, Benzophenon- und Benzotriazol-Derivaten;

E) eines oder mehrere Verdünnungsmittel, ausgewählt unter den Paraffinen und Cycloparaffinen, die bei Raumtemperatur flüssig sind oder einen Schmelzpunkt unterhalb 110 °C besitzen, epoxidiertem Sojabohnen- oder Leinsamenöl, Siliconölen und Olefinoligomeren in einer Menge von nicht mehr als 0,3%.

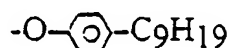
2. Verfahren nach Anspruch 1, worin die Olefinpolymeren aus der Gruppe ausgewählt sind von:

- (1) isotaktischem oder vorwiegend isotaktischem Polypropylen;
- (2) HDPE-, LLDPE-, LDPE-Polyethylen;
- (3) kristallinen Copolymeren des Propylens mit Ethylen und/oder anderen geradkettigen oder verzweigten C<sub>3-8</sub>- $\alpha$ -Olefinen;
- (4) elastomeren Ethylen/C<sub>3-8</sub>- $\alpha$ -Olefin-Copolymeren und elastomeren Ethylen/C<sub>3-8</sub>- $\alpha$ -Olefin/Dien-Terpolymere mit einem geringeren Anteil an Dien, wobei das  $\alpha$ -Olefin unter Propylen, 1-Buten, 1-Penten, 1-Hexen, 4-Methyl-1-penten und 3-Methyl-1-buten ausgewählt ist;
- (5) heterophasischen Polymeren, umfassend (A) eine Homopolymerfraktion von Propylen oder einem der unter Punkt (3) definierten Copolymeren und eine Copolymerfraktion (B) der unter Punkt (4) definierten elastomeren Copolymeren.

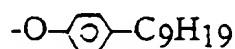
3. Verfahren nach Anspruch 1, worin die Stabilisatoren (A) ausgewählt sind unter Distearylpentaerythrit-diphosphit, 4,4'-Butyliden-bis-(3-methyl-6-tert.-butylphenyl-di-tridecyl)-phosphit, Tri-(monononylphenyl)-phosphit und Verbindungen der folgenden Formeln:



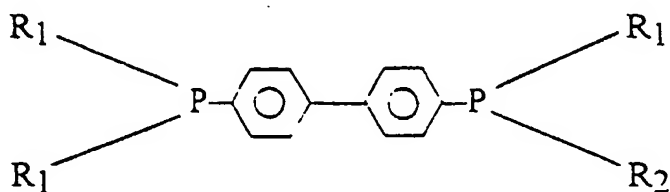
worin R<sub>1</sub> und R<sub>2</sub> beide Reste -O-C<sub>4</sub>H<sub>9</sub>, -O-C<sub>8</sub>H<sub>17</sub>(iso) oder



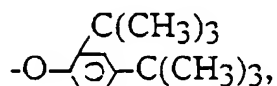
sind oder eine der beiden Gruppen R<sub>1</sub> und R<sub>2</sub> ein Rest

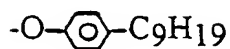


ist, während die andere ein Rest -O-C<sub>4</sub>H<sub>9</sub> oder -O-C<sub>8</sub>H<sub>17</sub>(iso) ist;

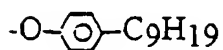


worin R<sub>1</sub> und R<sub>2</sub> beide Reste -O-C<sub>4</sub>H<sub>9</sub>, -O-C<sub>8</sub>H<sub>17</sub>(iso),

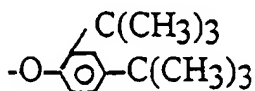




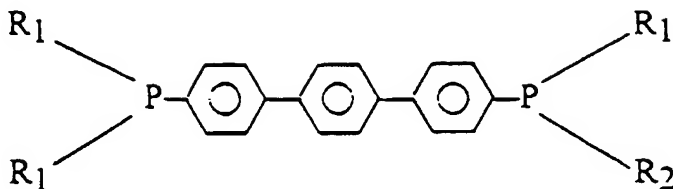
sind oder  $\text{R}_1$  ein Rest



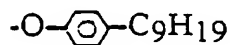
ist und  $\text{R}_2$  ein Rest  $-\text{O}-\text{C}_8\text{H}_{17}$ ,  $-\text{O}-\text{C}_8\text{H}_{17}(\text{iso})$  oder  $-\text{O}-\text{C}_4\text{H}_9$  ist oder  $\text{R}_1$  ein Rest



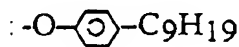
ist und  $\text{R}_2$  ein Rest  $-\text{O}-\text{C}_4\text{H}_9$  ist;



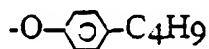
worin  $\text{R}_1$  und  $\text{R}_2$  beide Reste  $-\text{O}-\text{C}_8\text{H}_{17}$  oder



sind oder  $\text{R}_1$  ein Rest



ist und  $\text{R}_2$  ein Rest

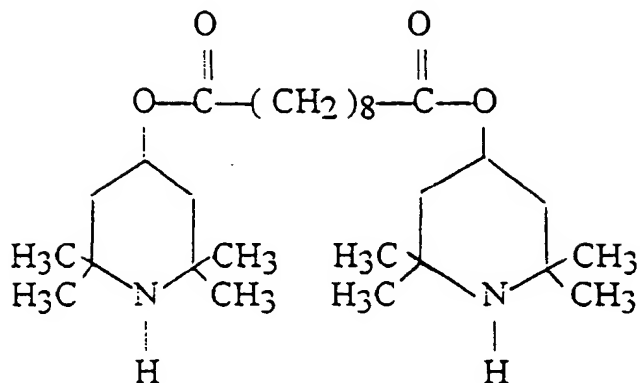


ist.

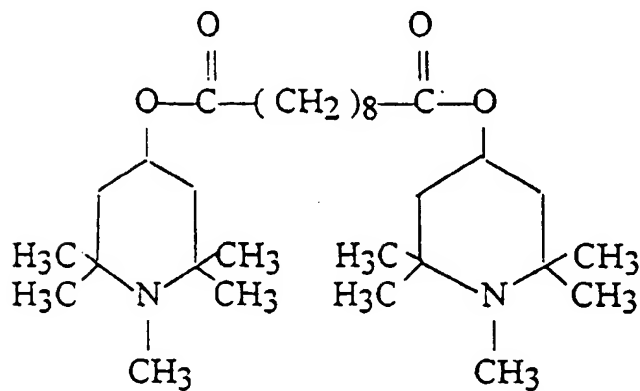
4. Verfahren nach Anspruch 1, worin die Stabilisatoren (B) ausgewählt sind aus der Gruppe von 2,6-Di-tert.-butyl-4-methylphenol, 2,2-Bis-(4-(2-(3,5-di-tert.-butyl-4-hydroxyhydrocinnamoyloxy))-ethoxyphenyl)-propan und Octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionat.
5. Verfahren gemäß Anspruch 1, worin die Komponenten (C) ausgewählt sind aus der Gruppe von Dilauryl-thiodipropionat, Distearyl-thiodipropionat und Verbindungen der allgemeinen Formel (IX)  $\text{R}-\text{S}-\text{S}-\text{R}$ , worin die Reste R, die gleich oder verschieden sind, Alkyl-, Aryl- oder Aralkylreste mit 1 bis 20 Kohlenstoffatomen sind.
6. Verfahren nach Anspruch 1, worin die Lichtstabilisatoren (D) ausgewählt sind aus der Gruppe der Verbindungen

der Formeln:

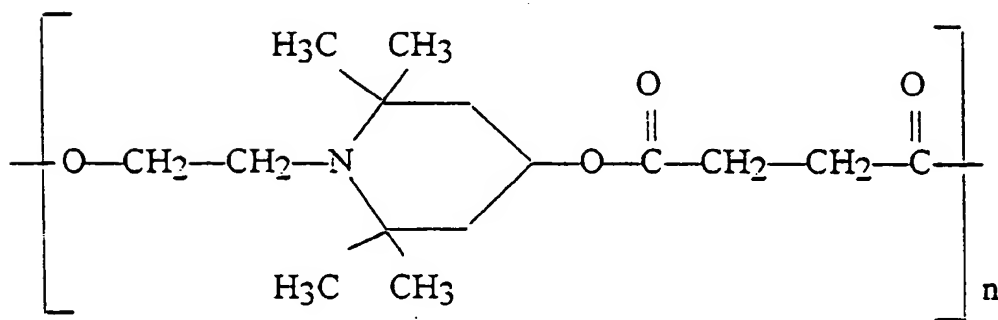
XI



XII

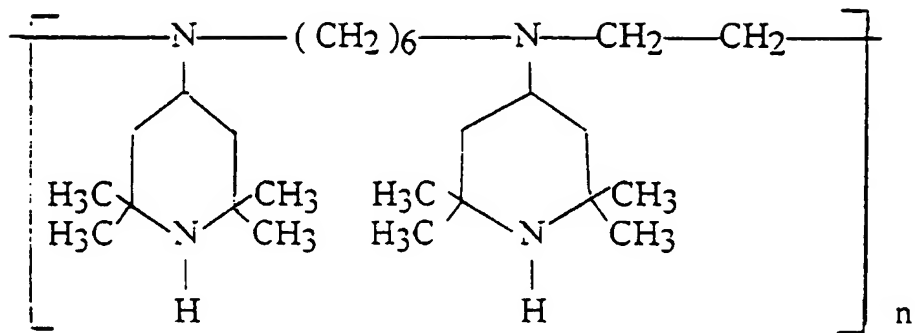


XIII

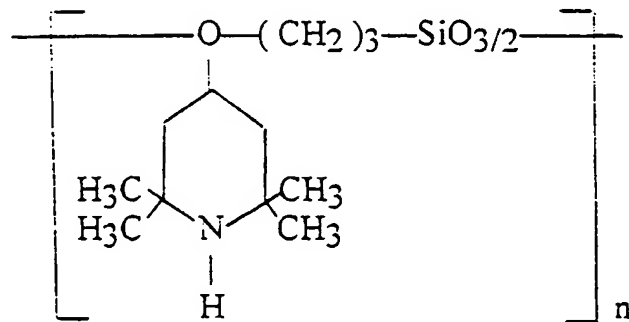


worin n einen Wert von 2 bis 10 besitzt,

XIV



XV



worin n einen Wert von 2 bis 100 besitzt, 2-Hydroxy-4-n-octyloxy-benzophenon und 2-(2'-Hydroxy-3'-tert.-butyl-5'-methylphenyl)-5-chlorbenzotriazol.

7. Verfahren gemäß Anspruch 1, worin als Verdünnungsmittel (E) mikrokristalline Paraffinwachse mit einem Schmelzpunkt von 60 bis 90 °C verwendet werden.

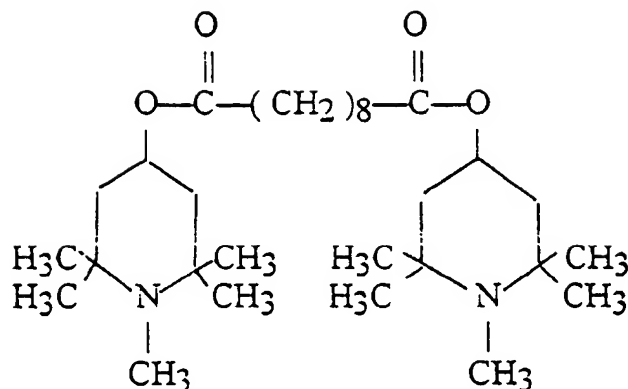
8. Verfahren nach Anspruch 1, worin die flüssige Mischung die folgenden Stabilisatoren umfaßt:

A) Tetrakis-(2,4-di-tert.-butylphenyl)-4,4'-diphenylylen-diphosphonit;

B) Pentaerythrit-tetrakis-(3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propanoat) und gegebenenfalls Octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionat,

und gegebenenfalls

D) den gehinderten Amin-Lichtstabilisator der Formel XII



und

E) eines oder mehrere Verdünnungsmittel.

9. Verfahren gemäß Anspruch 1, worin die flüssige Mischung auf den Polymerteilchen mit einer Temperatur von geringer als 50 °C abgeschieden wird.

## Revendications

1. Un procédé de préparation de particules de polymère d'oléfine stabilisée non extrudée, ledit procédé comprenant l'étape de polymérisation d'un ou plusieurs monomères oléfiniques en présence d'un catalyseur de Ziegler-Natta, pour obtenir ainsi directement des particules de polymère d'oléfine ayant une forme sphéroïdale et, ensuite, l'étape de dépôt d'un mélange stabilisant sur la surface desdites particules de polymère, ledit mélange de stabilisant étant soit un mélange fondu, soit un mélange dans lequel au moins le constituant (A) est à l'état liquide, ne contenant aucun solvant, et comprenant les stabilisants suivants (pourcentage en poids par rapport au poids de particules de polymère) :

A) de 0,02 % à 0,15 % d'un ou plusieurs phosphites ou phosphonites organiques ou leurs mélanges qui sont liquides à la température ambiante ou présentent un point de fusion inférieur à 100°C ;

B) de 0,025 % à 0,02 % d'un ou plusieurs anti-oxydants phénoliques présentant un point de fusion de 45 à 130°C ;

et, le cas échéant, un ou plusieurs des constituants complémentaires suivants :

C) de 0,05 % à 0,5 % d'un ou plusieurs thioéthers ou polysulfures organiques ou leurs mélanges ;

D) de 0,1 % à 1,0 % d'un ou plusieurs stabilisants vis-à-vis de la lumière qui sont liquides à la température ambiante ou présentent un point de fusion inférieur à 150°C, choisis dans le groupe consistant en amine encombrée, dérivés de benzophénone et de benzotriazole stabilisant vis-à-vis de la lumière ;

E) un ou plusieurs diluants choisis dans le groupe consistant en paraffines et cycloparaffines qui sont liquides à la température ambiante ou présentent un point de fusion inférieur à 110°C, huile de soja ou huile de lin époxydées, huiles de silicone et oligomères d'oléfine, en une quantité ne dépassant pas 0,3 %.

2. Le procédé selon la revendication 1, dans lequel les polymères d'oléfine sont choisis dans le groupe consistant en :

1) polypropylène isotactique ou majoritairement isotactique ;

2) polyéthylène HDPE, LLDPE, LDPE ;

3) copolymères cristallins de propylène avec l'éthylène et/ou d'autres alpha-oléfines en C<sub>3</sub>-C<sub>8</sub> linéaires ou ramifiées ;

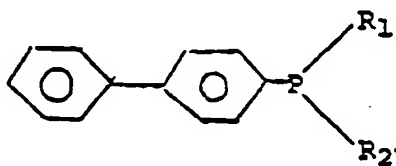
4) copolymères élastomères éthylène/alpha-oléfines en C<sub>3</sub>-C<sub>8</sub> et terpolymères élastomère éthylène/alpha-oléfine en C<sub>3</sub>-C<sub>8</sub>/diène, contenant des proportions mineures de diène, où l'alpha-oléfine est choisie parmi propylène, 1-butène, 1-pentène, 1-hexène, 4-méthyl-1-pentène, 3-méthyl-1-butène ;



5) polymères hétérophasiques comprenant :

(A) une fraction homopolymère de propylène ou d'un des copolymères définis en (3) et une fraction de copolymère (B) des copolymères élastomères définis dans (4).

3. Le procédé selon la revendication 1, dans lequel les stabilisants (A) sont choisis dans le groupe consistant en distéarylpentaérythrityl diphosphite ; 4,4'-butylidène bis(3-méthyl-6-tert-butylphényl-di-tridécyl)phosphite ; tri(monononylphényl)-phosphite et des composés répondant aux formules suivantes :

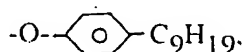


dans laquelle :

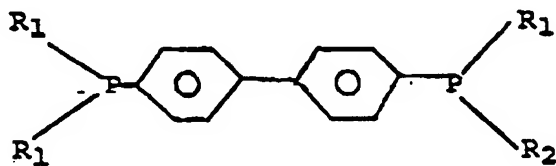
R<sub>1</sub> et R<sub>2</sub> sont l'un et l'autre des radicaux -O-C<sub>4</sub>H<sub>9</sub>, -O-C<sub>8</sub>H<sub>17</sub>(iso) ou



ou bien un ou deux groupes R<sub>1</sub> et R<sub>2</sub> sont un radical

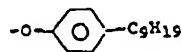
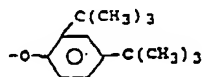


tandis que l'autre est un radical -O-C<sub>4</sub>H<sub>9</sub>, -O-C<sub>8</sub>H<sub>17</sub>(iso) ;



dans laquelle :

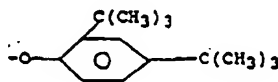
R<sub>1</sub> et R<sub>2</sub> sont l'un et l'autre des radicaux -O-C<sub>4</sub>H<sub>9</sub>, -O-C<sub>8</sub>H<sub>17</sub>(iso),



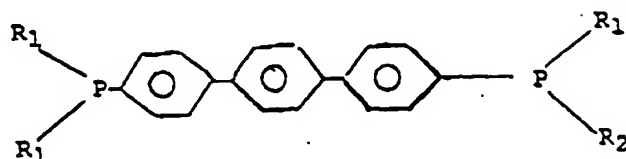
ou bien R<sub>1</sub> est un radical



et  $R_2$  est un radical  $-O-C_8H_{17}$ ,  $-O-C_8H_{17}(iso)$ , ou bien  $-O-C_4H_9$ , ou bien  $R_1$  est un radical



et  $R_2$  est un radical  $-O-C_4H_9$  ;



dans laquelle :

$R_1$  et  $R_2$  sont l'un et l'autre des radicaux  $-O-C_8H_{17}$ , ou



ou bien  $R_1$  est un radical



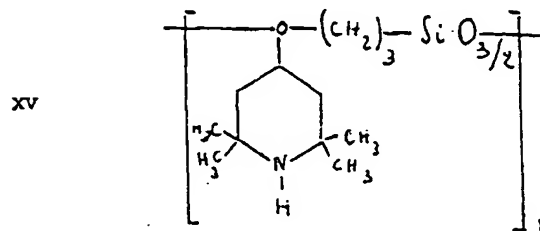
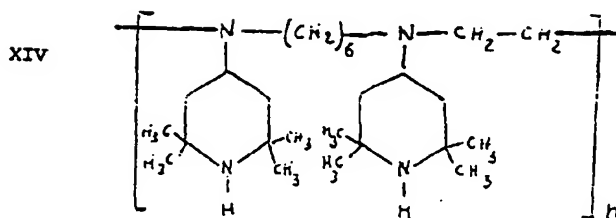
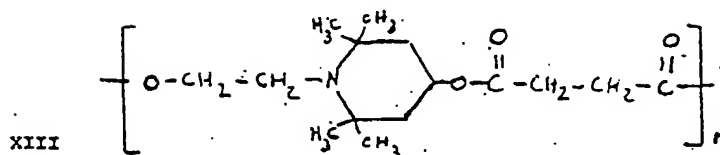
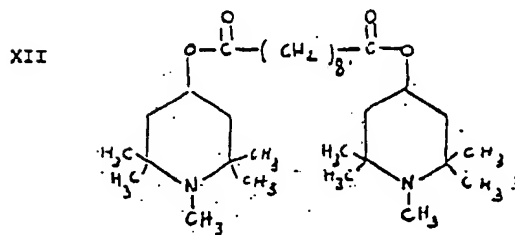
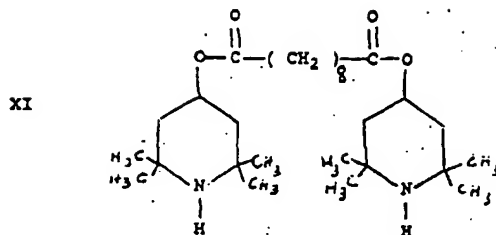
et  $R_2$  est un radical



4. Le procédé selon la revendication 1, dans lequel les stabilisants (B) sont choisis dans le groupe consistant en 2,6-di-tert-butyl-4-méthylphénol, 2,2-bis(4-(2-(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyloxy)éthoxyphényl)propane et octadécyl-3-(3,5-di-tert-butyl-4-hydroxyphényl)-propionate.

5. Le procédé selon la revendication 1, dans lequel les constituants (C) sont choisis dans le groupe consistant en dilaurylthiodipropionate ; distéarylthiodipropionate et les composés répondant à la formule générale (IX)  $R-S-S-R$ , où les radicaux R, identiques ou différents, sont des radicaux alkyle, aryle ou aralkyle comportant 1 à 20 atomes de carbone.

6. Le procédé selon la revendication 1, dans lequel les stabilisants vis-à-vis de la lumière (D) sont choisis dans le groupe consistant en les composés répondant aux formules :



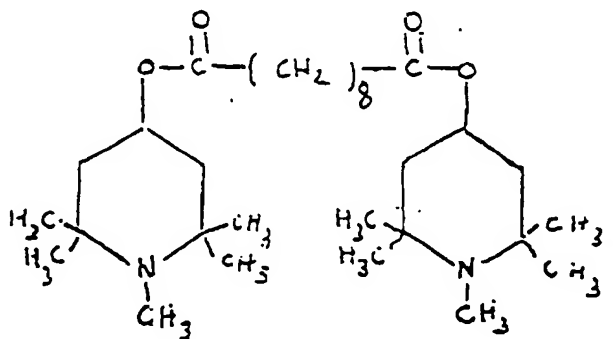
où n vaut de 2 à 10,

n vaut de 2 à 100.

2-hydroxy-4-n-octyloxy benzophénone et 2-(2'-hydroxy-3'-tert-butyl-5'-méthylphényl)-5-chlorobenzotriazole.

7. Le procédé selon la revendication 1, dans lequel, en tant que diluant (E), on utilise des cires de paraffine micro-cristallins présentant un point de fusion de 60°C à 90°C.

A) tétrakis-(2,4-di-tert-butylphényl)-4,4'-diphénylène diphosphonite ;  
B) pentaérythrityl tétrakis(3-(3,5-di-tert-butyl-4-hydroxyphényl)-propanoate), et, le cas échéant, octadécyl-3-(3,5-di-tert-butyl-4-hydroxyphényl)-propionate ; et, le cas échéant,  
D) les amines encombrées stabilisantes vis-à-vis de la lumière de formule (XII) :



9. Le procédé selon la revendication 1, dans lequel le mélange liquide est déposé sur des particules de polymère ayant une température non inférieure à 50°C.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**